Effect of Lanthanide (La(III))-Containing Ionomer on Thermal Stabilization of Poly(vinyl chloride)

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ABSTRACT: A type of lanthanide (La(III))-containing ionomer based on acrylate processing aid (ACR) for poly (vinyl chloride) (PVC) was synthesized, and influence of the ionomer on thermal stabilization of PVC was investigated with visual color comparison and Congo red methods. Results revealed that the ionomer with a suitable La(III) content behaved as a good costabilizer to PVC. It was able to extend static stabilization time of PVC and postpone "zinc burning." The stabilizing efficiency of the ionomer to PVC depended on ion content, which was discussed in terms of Eisenberg–Hird–Moore model. Moreover, Fourier transform infrared test verified that this ionomer can react with zinc stearate ($ZnSt_2$) to form some new structures, which is responsible for postponing "zinc burning." The ionomer and epoxidized soybean oil exhibited a synergistic effect on the stabilizing efficiency of calcium stearate ($CaSt_2$)/$ZnSt_2$ stabilizer to PVC compounds. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: PVC; La(III)-containing ionomer; costabilizer

INTRODUCTION

As an important commercial resin, poly(vinyl chloride) (PVC) ranks the second among the thermoplastics in terms of total worldwide production volume. However, thermal degradation resulted from inherent structural defects of PVC seems to be inevitable during thermal processing.[1–3] A variety of stabilizers have been explored to trap the released hydrochloric acid (HCl) and to prohibit further degradation by preventive reactions during processing, which restrains severe discoloration and loss of physical properties.[2–6] In respect to environmental protection and health, attentions have been paid to Ca/Zn stabilizers.[2,3] Although Ca/Zn stabilizers have a synergistic effect on stabilizing PVC, they have some disadvantages in long-term stabilization due to their marked "zinc burning." Epoxidized soybean oils (ESBO)[2,3,7] or polyols[2,3,8] are usually used as costabilizers to improve the stabilizing efficiency. Nevertheless, most of these products are low-molecular weight compounds exhibiting tendency of migration and fogging.[9,10] Increasing molecular weight of processing aids is one of effective ways to avoid this disadvantage. However, to our knowledge, only a few researches on polymeric costabilizers have been reported.[9,11]

Ionomers, containing a relatively small amount of ionic groups along backbone chains, have been used widely and investigated excessively[12–20] due to their excellent properties, although the exact morphologies of aggregates in ionomers have not been fully elucidated.[12,13,21,22] It is worth noting that a number of functional groups such as sodium, zinc, and calcium carboxylates in ionomers may absorb HCl and interact with polar compounds (e.g., carboxylic salts), which makes ionomers to be a sort of potential polymeric costabilizer.[23]

Rare earth compounds have been applied as environment-friendly costabilizers to PVC.[24–26] Acrylate processing aid (ACR), usually used to promote PVC fusion,[27] is poly(methyl methacrylate-*co*-butyl methacrylate-*co*-styrene) copolymer containing more than 90 wt % methyl methacrylate (MMA) unit. We have synthesized a kind of ACR-based ionomer named ACR-*X* [*X* represents weight percentage of lanthanide (La(III)) in the ionomer]. ACR in the ionomer endows it with good compatibility with PVC,[28–30] and carboxylic La(III) in the ionomer could stabilize PVC.[11] However, the costabilization mechanism of ACR-*X* for PVC compounds has not been discussed thoroughly in our previous work. We, in this work, investigate this mechanism especially the reason for the synergistic effect between ACR-*X* and zinc stearate incorporated in PVC.

EXPERIMENTAL

Materials

PVC (SG5) and ACR (401) were supplied by Hangzhou Chuanhua Co., Zhejiang, China and Zhiqiang Plastic Aids Plant, Shanghai, China, respectively. Hydrated lanthanum chloride ($LaCl_3 \cdot nH_2O$) and ESBO were obtained from Sinopharm Chem. Reagent Co., Shanghai, China, and Aladdin Reagent Database, Shanghai, China, respectively. Zinc and calcium stearates ($ZnSt_2$ and $CaSt_2$) from Wenzhou Chem. Reagent Plant, Zhejiang, China was used as primary and secondary stabilizers, respectively. Glyceryl monostearate from Hangzhou Chuanhua Co., Zhejiang, China and paraffin wax from Shanghai Specimen and Model Factory, Shanghai, China were added into formula as lubricants. All other reagents were of analytical grade.

Preparation of ACR-X

ACR was partially hydrolyzed according to the method described in Ref. [31]. The partially hydrolyzed ACR was filtered and washed several times with ethanol and was then suspended in ethanol. Appropriate amount of HCl was dropped into the suspension to neutralize sodium hydroxide remained from hydrolyzation and recover the hydrolyzed ACR to acid form. The acidified ACR was filtered and then suspended in ethanol. An ethanol solution of $LaCl_3$ was dropped into the suspension, and the mixture was vigorously stirred at room temperature for 48 h at pH = 5.5. Solid ionomer ACR-X was obtained after removing the remaining $LaCl_3$ using excess water and was dried under vacuum at 70°C for 48 h. La(III) content in the ionomer was determined using Inductively Coupled Plasma-Atomic Emission Spectrometry.

Preparation of PVC compounds

One series of samples were prepared by mixing 100 phr (per hundred resin) PVC with 0.3 phr paraffin wax, 0.5 phr $CaSt_2$, 2 phr glyceryl monostearate, 4 phr dioctylphthalate, and 4 phr stabilizers (ACR-X/$ZnSt_2$ with 9 : 1, 7 : 1, 4 : 1, and 3 : 1 weight ratios) at 180°C in a Brabender torque rheometer (Brabender, Germany) at 35 rpm for 5 min. Another series of samples were prepared by adding 3 phr ESBO into the above formula according to the same processing procedure. The mixtures were compression molded at 14.7 MPa and 180°C for 5 min. Square samples (20 × 20 mm) for visual color comparison test were cut from the compression sheets. The compression sheets were fragmentized into powders for Congo red test.

Measurements

To investigate the stabilizing efficiency of ACR-X itself, Congo red test was performed to a mixture of 2.5 g virgin PVC powder and 0.1 g ACR-X. The possible synergistic effect between ACR-X and $CaSt_2$/$ZnSt_2$ or $CaSt_2$/$ZnSt_2$/ESBO complex stabilizers was examined through Congo red test to 5 g PVC compound powder processed aforementioned. According to ASTM D4202, the powders were put into a tube with Congo red test paper located at 2.5 cm above the sample. The tube was heated in a glycerol bath at 180°C to evaluate static thermal stabilization time (t_{ss}) defined as the time when Congo red test paper began to turn blue.

Square PVC sheets (20 × 20 mm) were heated in a thermal aging test oven at 180°C. Static thermal aging was performed according to ISO 305-1990 (E). The sheets were taken out every 5 min.

The synergistic effect between ACR-X and $ZnSt_2$ was analyzed using Fourier transform infrared (FTIR) spectra. About 1.0 mg sample was ground together with ~ 200 mg dried potassium bromide powder in an agate bowl. The mixture was pressed into transparent slice under ~ 400 kg/cm^2 pressure. FTIR spectra were measured using a VECTOR 22 spectrometer (Bruker, Germany) with a scan-co-addition of 40 and a resolution of 1 cm^{-1}.

Differential scanning calorimetry (DSC) thermograms were recorded using a differential scanning calorimeter (Q100, TA Instruments-Waters LLC, USA), which was calibrated using indium before measurement. The measurements of about 10 mg sample packed into an aluminum pan were performed under dry nitrogen flow of ~ 50 mL/min at a scanning rate of 10°C/min.

A metal pocket technique has been used in dynamic mechanical thermal analysis (DMTA) for determining glass transitions of powder samples, which are difficult to be molded into a certain shape.[32,33] The dynamic modulus measured from this method reflects the combination of both sample and metal pocket. This method is useful for identifying thermal transitions of the sample from loss factor tan δ curve only if the metal pocket does not show any thermal transition within the tested temperature ranges. The ACR-X powders were distributed evenly inside the pockets (10 mm in length, 7.5 mm in width, and 1 mm in thickness) and the pockets folded shut. DMTA was performed at 1 Hz with a dynamic mechanical thermal analyzer (Q800, TA Instruments-Waters LLC, USA) with a single cantilever bending mode over the temperature range from 40 to 300°C at a heating rate of 5°C/min. Because the dynamic modulus did not reflect the material properties of ACR-X, only tan δ curve was reported in this work.
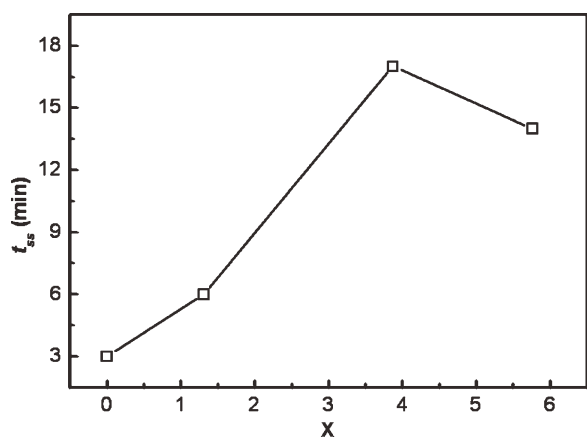
Figure 1 Influence of La(III) content in the ACR-X ionomer on tss at 180°C for PVC powder dry-blended with ACR-X.

RESULTS AND DISCUSSION

Influence of ACR-X on t_{ss}

Figure 1 shows the influence of La(III) content (X) in ACR-X on t_{ss} of the mixture of 2.5 g virgin PVC powder and 0.1 g ACR-X. ACR-X can improve t_{ss} markedly and t_{ss} reaches maximum at $X = 3.87\%$, revealing that X plays an important role in stabilizing PVC.

According to Eisenberg–Hird–Moore model[18,34] for amorphous random ionomers, ionic groups in ionomers tend to form multiplet aggregates, due to the strong interaction among ionic groups and the difference in polarity values between the ionic groups and the nonpolar polymer matrix. At low-ion contents, only multiplets are formed, acting as crosslinks. The mobility of polymer chains surrounding the multiplets is restricted, leading to increases in modulus and glass transition temperature (T_{g1}) of the matrix. These restricted regions start to overlap as ion content increases. Once the size of the overlapped regions are larger than a certain dimension, for example, 10 nm, these regions constitute and behave as phase-separated regions, exhibiting their own glass transition temperature (T_{g2}).[18] Moussaif et al.[35] studied the miscibility between MMA-co-zinc acrylate copolymer and poly(vinylidene fluoride). The blends containing half-neutralized copolymer exhibit miscibility and mechanical property better than those containing non-neutralized and all-neutralized copolymers. These could be attributed to association of zinc carboxylate groups into multiplets and/or clusters rather than to specific intermolecular interactions. Zinc carboxylates are most likely to form clusters at 100% neutralization.[36,37] Okamoto et al.[31,38] reported that salts of styrene-acrylic acid and MMA-methacrylic acid copolymers displayed a typical fluorescence concentration quenching behavior, reaching maximum at 6 and 4–6 wt % metal

contents, respectively. The metal content in the copolymer falls within the same range where ion cluster starts to form. The europium (III) and terbium (III) ions are closely located together in aggregates of the copolymers. These investigations show that the appearance of cluster has a strong influence on the performance of the ionomers. The t_{ss} maximum in Figure 1 might be ascribed to the aggregation of ionic groups in ACR-X. To testify this speculation, we investigate the thermal transition behaviors of ACR-3.87 and ACR-5.76 using DMTA.

Figure 2 shows loss tangent (tan δ) as a function of temperature for ACR-3.87 and ACR-5.76. There is only one relaxation peak at 186°C on the curve of ACR-3.87, which corresponds to the T_{g1} peak. Two peaks appear at 214 and 282°C on the curve of ACR-5.76, which are assigned to T_{g1} and T_{g2}, respectively. T_{g1} of ACR-5.76 is about 30°C higher than that of ACR-3.87 due to the higher multiplet density associated with higher ion content. The curve of ACR-3.87 warps up at the end of scan, seeming to be raise of baseline rather than appearance of cluster peak,[39] because T_{g2} increases almost linearly with ion content.[12–15,36] In PVC compounds, the formation of cluster in ACR-X will lead to a decrease of effective number of stabilizing functional group (ENSFG) to trap HCl and to complex with ZnSt$_2$, thereby lowering the stabilizing efficiency of ACR-5.76 in comparison with ACR-3.87.

At low temperatures, ion pairs and the polymer chains attached on them tend to associate and aggregate tightly and even form some ordered packing of ionic groups inside the aggregates.[40] Migration of ion pairs between multiplets, say, "ion hopping," occurs at elevated temperatures,[33,41,42] despite the fact that some of the multiplets still exist as evidenced by a small-angle X-ray peak.[22,43,44] The ion hopping begins at temperature range of $T_{g1} - T_{g1} + 25°C$,[41,42] being much lower than T_{g2}.[39] The cations
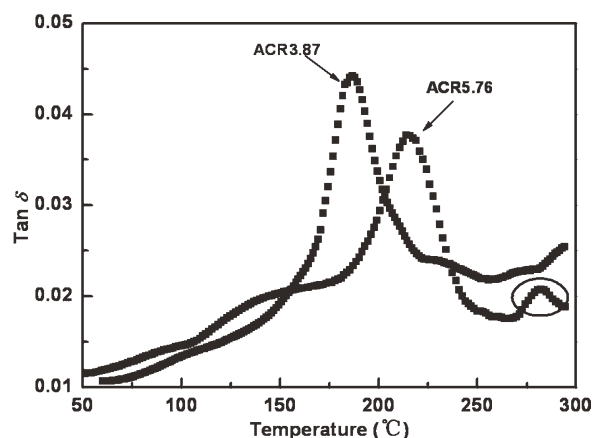

Figure 2 Loss tangent (tan δ) as a function of temperature for ACR-3.87 and ACR-5.76 measured at 1 Hz.
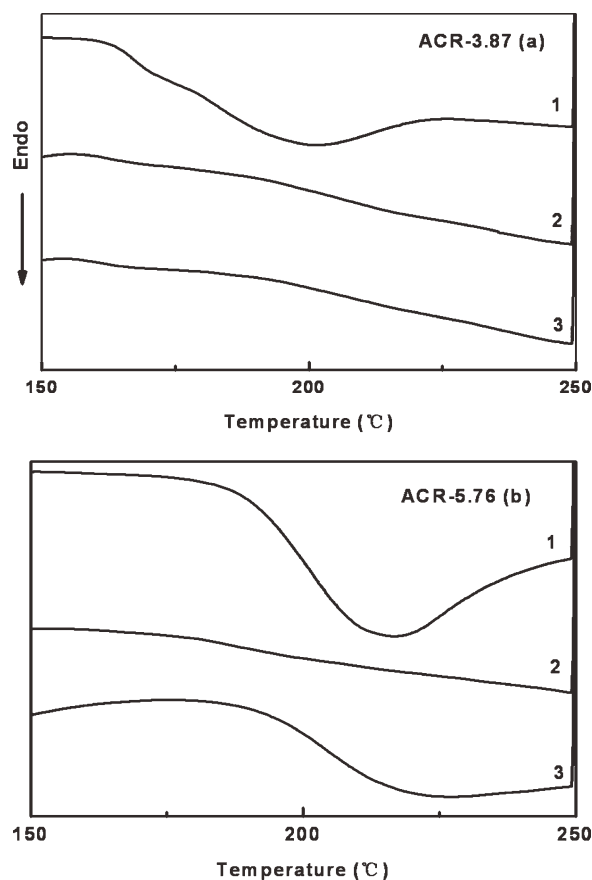
Figure 3 DSC curves for ACR-3.87 (a) and ACR-5.76 (b) recorded during the first (curve 1) and the second heating scans (curve 2) of the as-prepared sample and the first heating scan (curve 3) of the sample annealing at 180°C for 20 min.

may migrate as Fickian diffusion in form of ion pairs,[45] followed by an increase in expansion coefficient[42] and even by an order–disorder transition,[46–48] which makes the rigid ionic aggregate regions soften, partly losing their functionality.[41,42] The longer relaxation time of the cluster hinders the ion hopping[49] and affect the interaction between ACR-X and HCl or ZnSt$_2$. If the clusters in ACR-5.76 relax quickly enough, the stabilizing functional groups can be released in a negligibly time, and the t_{ss} maximum could hardly be attributed to the appearance of cluster.

We used DSC to analyze ACR-X annealed at 180°C for investigating the effect of heat-treatment on the relaxation. Figure 3 presents DSC thermograms of ACR-3.87 and ACR-5.76 undergoing different heat-treatments. On the first heating of the as-prepared samples, both ACR-3.87 and ACR-5.76 exhibit a broad transition with onset temperatures of T_{g1} at 162 and 179°C, respectively. A distinct broad endothermic peak can be observed, which corresponds to relaxation of chain segments stretched by the aggregated ionic species.[42,50] This peak is absent on the subsequent cooling and also on an immediate

subsequent heating run, indicating that the restriction due to the multiplets or clusters becomes weak after the thermal scan. The ACR-3.87 and ACR-5.76 samples annealed at 180°C for 20 min show heating thermograms different to the as-prepared samples. No endothermic peak can be observed on the thermogram of the annealed ACR-3.87 while the annealed ACR-5.76 shows an endothermic peak with transition temperature higher than the as-prepared ACR-5.76. The ion groups in cluster of ACR-5.76 are packed tightly, and they need longer time or higher temperature to be released as effective stabilizing functional groups. The formation of cluster tends to reduce ENSFG in ACR-X at processing temperatures, which evidently influences the stabilization efficiency to PVC.

Influence of ACR-X on t_{ss} of PVC compounds containing CaSt$_2$/ZnSt$_2$

Figure 4 shows influence of X on t_{ss} of PVC compounds containing 4 phr ACR-X/ZnSt$_2$ complex stabilizers with different ratios as indicated. ACR-X improves t_{ss} markedly in comparison with $X = 0$ representing unmodified ACR. For ACR-X/ZnSt$_2$ ratios of 9/1 and 7/1, t_{ss} levels off at $X \geq 3.87\%$. For ACR-X/ZnSt$_2$ ratio of 7/1, t_{ss} at $X > 2.50\%$ is extended more than one time in comparison with $X = 0$. At ACR-X/ZnSt$_2$ ratios of 3/1 and 4/1, t_{ss} reaches maximum at $X = 3.87\%$. At the same X value, decreasing ACR-X/ZnSt$_2$ ratio leads t_{ss} to decrease remarkably due to intensified "zinc burning".

Long-chain fatty acids and their derivatives are widely used as plasticizers to reduce melt viscosity of ionomers by soaking into the multiplets and clusters and by interacting with ion groups of ionomer.[51–53] Below the melting point, they may behave as filler for enhancing physical property of the ionomer. ACR-X might exhibit synergistic effect with ZnSt$_2$ for stabilizing PVC. ACR-X/ZnSt$_2$ (7/1) mixture was thermally treated at 180°C, and the
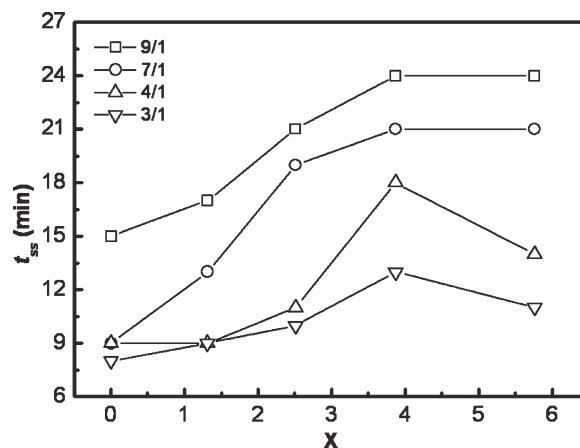

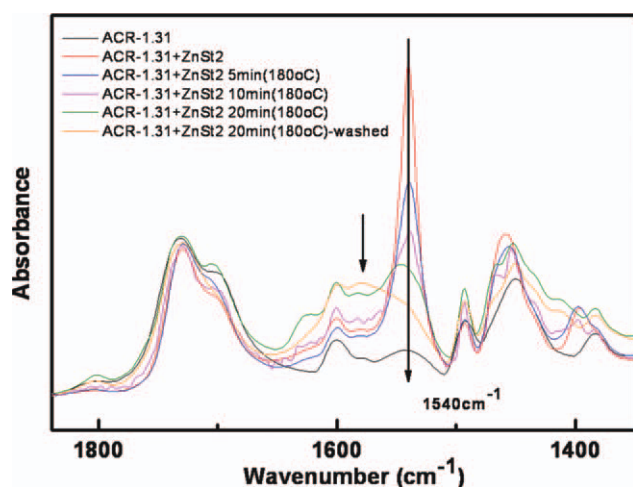**Figure 4** t_{ss} at 180°C as a function of X for PVC compounds.

Figure 5 Scale-expanded FTIR spectra of ACR-1.31/ZnSt2 mixture in 1850–1350 cm^{-1}: black, ACR-1.31; red, ACR-1.31 dry-blended with ZnSt2; blue, pink and green, ACR-1.31/ZnSt2 mixture annealed at 180°C for 5, 10, and 20 min, respectively; orange, the mixture annealed at 180°C for 20 min and washed with hot ethanol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

synergistic effect between ACR-X and ZnSt$_2$ was investigated using FTIR spectra.[54,55]

There is a small amount of styrene unit in ACR. The absorbance of styrene almost remains unchanged during thermal treatments. The spectra are displayed scale-expanded to the absorbance of bending vibration of external plane of C—H of benzene ring (700 cm^{-1}) as an internal standard. Because spectra of ACR-X/ZnSt$_2$ mixtures with different ratios were similar, only the ACR-1.31 mixture is shown in Figure 5 as an example. In comparison with original ACR and partially hydrolyzed ACR (not shown), ACR-X exhibits a mild broad peak centered at 1540 cm^{-1} attributed to asymmetric carboxylate stretching vibration, $v_{as}(COO^-)$, of La(III) salt in eight-coordination.[56] The absorbance of this peak increases nearly proportionally with increasing X. Upon addition of ZnSt$_2$, this peak is covered by a strong sharp peak from $v_{as}(COO^-)$ vibration of Zn(II) salt at the same wavenumber range. As the annealing time increases, the Zn(II) peak becomes weaker gradually and shifts to high wavenumbers. Meanwhile, the absorbance in the nearby range becomes more intense and broader. Neither ACR-X nor ZnSt$_2$ show the same variation after annealing. These indicate that soaking of ZnSt$_2$ into ACR-X and interaction between ZnSt$_2$ and ion groups of ACR-X may lead to reorganization of the multiplets and clusters during annealing. Figure 6 shows absorbance intensity ratio A_{1540}/A_{700}. The ratio of ACR-X/ZnSt$_2$ mixtures all decreases with increasing annealing time.

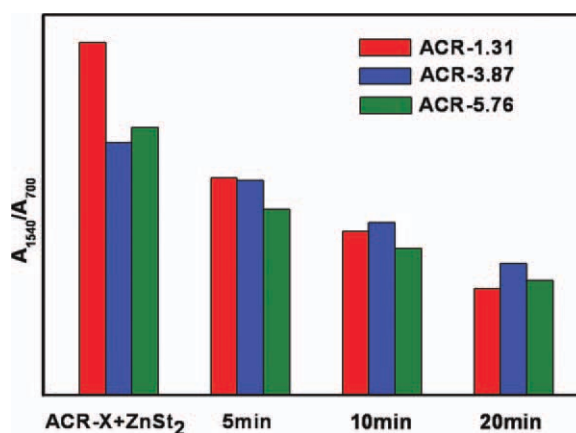Figure 7 shows the absorbance area ratio of the $v_{as}(COO^-)$ to the 700 cm^{-1} peak (Area$_{1540}$/Area$_{700}$)

Figure 6 Influence of annealing time on absorbance ratio A1540/A700 for the ACR-X/ZnSt2 mixture annealed at 180°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

for the ACR-X/ZnSt$_2$ mixture annealed at 180°C for 20 min. Area$_{1540}$/Area$_{700}$ becomes larger after annealed. Although ACR-5.76 has more ionic groups than ACR-3.87 to interact with ZnSt$_2$, their Area$_{1540}$/Area$_{700}$ values are almost the same, indicating that the clusters may hinder the interaction between ion groups of ACR-5.76 and ZnSt$_2$. Washing the annealed sample with hot alcohol can remove free ZnSt$_2$ in the mixture and reduce the $v_{as}(COO^-)$ absorbance. However, the $v_{as}(COO^-)$ peak is still stronger and broader than that of original ACR-X, indicating that some ZnSt$_2$ reacts with ion groups in ACR-X to form complex. This complex is similar to that mentioned in Refs. 57 and 58 and may be responsible for the synergistic effect observed as remarkable improvement of t_{ss} in PVC compounds containing both ACR-X and CaSt$_2$/ZnSt$_2$ stabilizers. The difference of Area$_{1540}$/Area$_{700}$ between ACR-X and the ethanol-washed mixture could be used to represent the amount of complex generated from the
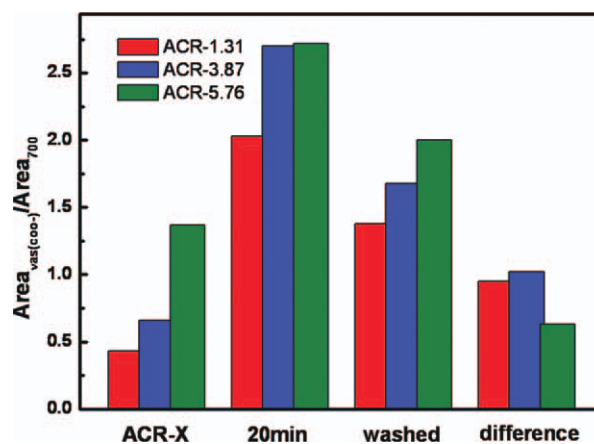

Figure 7 Influence of washing on Areavas(COO-)/Area700 for the ACR-X/ZnSt2 mixture annealed at 180°C for 20 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
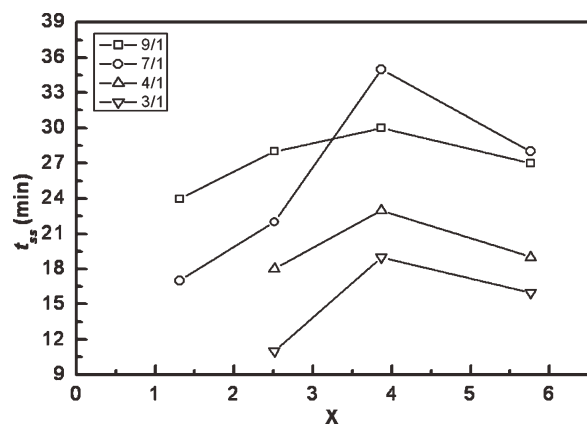
Figure 8 Influence of X on t_{ss} at 180°C for PVC compounds containing 3 phr ESBO.

reaction between ACR-X and ZnSt$_2$. The difference of ACR-3.87 is larger than the others, revealing that ACR-3.87 forms most complex with ZnSt$_2$, and the cluster formation in ACR-5.76 greatly reduces ENSFG at 180°C. This is one of the main reasons for the most marked improvement in t_{ss} for PVC containing ACR-3.87, as shown in Figure 4.

Influence of ESBO on stabilizing efficiency of ACR-X for PVC containing CaSt$_2$/ZnSt$_2$

ESBO is sometimes used together with Ca/Zn stabilizers for improving the processibility of PVC and postponing "zinc burning."[2,3,7] Figure 8 shows influ-

ence of ESBO on t_{ss} of PVC containing ACR-X and CaSt$_2$/ZnSt$_2$ stabilizers. In comparison with Figure 4, ESBO has no profound effect on the efficiency of unmodified ACR(X = 0)/Zn stabilizer. Addition 3 phr ESBO to PVC containing higher Ca/Zn contents only leads t_{ss} to increase by 3–5 min (not shown). Therefore, ACR-X is more effective than ESBO for improving the stabilization efficiency of Ca/Zn stabilizer. As shown in Figure 8, t_{ss} of the PVC compounds containing 3 phr ESBO exhibits similar variation with respect to X to those free of ESBO (Fig. 4). Addition ESBO brings about a remarkable increase in t_{ss} except for the compounds containing ACR or ACR-1.31. At ACR-X/ZnSt$_2$ ratios of 3/1 and 4/1, ESBO addition to the compounds containing ACR or ACR-1.31 accelerates "zinc burning." Otherwise, ESBO is very effective to improve the stabilization of PVC compounds containing ACR-3.87 and ACR-5.76. When ESBO and ACR-X are used together in the PVC compounds containing Ca/Zn stabilizer, the improvement on t_{ss} is significantly greater when compared with the addition of ESBO and ACR-X alone.

ESBO as a low-polarity plasticizer could decrease and broaden the T_{g1} transition of ionomer, which might improve mobility of the continuous phase to accelerate relaxation of the clusters.[12,14,15,59] For the ionomer with a low content of ion groups, most of the ion groups exist as isolated form and behave as effective stabilizing functional groups. The plasticization effect of ESBO is not apparent. On the other hand, the plasticization effect of ESBO weakens the ion
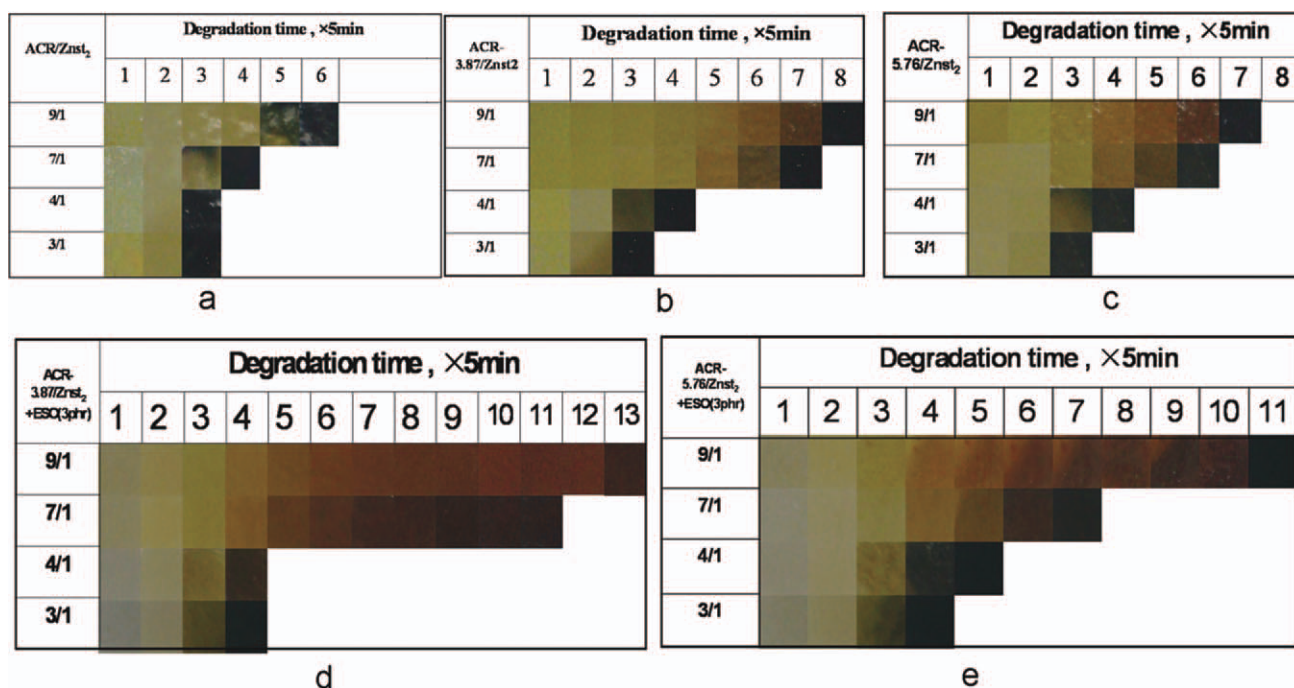

Figure 9 Color evolution as a function of time at 180°C for PVC strips with 4 phr ACR-X/ZnSt2 stabilizers at different ratios as indicated (a, b, and c) or 4 phr ACR-X/ZnSt2 stabilizers plus 3 phr ESBO (d and e). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

association in the ionomer with high ion contents and increases ENSFG, facilitating ACR-X to interacting with $ZnSt_2$ and HCl so as to stabilize PVC. However, the ESBO can hardly penetrate into the cluster phase to release more ENSFG so that the t_{ss} of PVC compounds containing ACR-5.76 is less than ACR-3.87.

Figure 9 shows the color evolution as a function of time for PVC strips at 180°C. For the control sample containing ACR/$ZnSt_2$, the time of PVC strips turning black decreases significantly with decreasing ACR/$ZnSt_2$ ratio [Fig. 9(a)] due to the intensified "zinc burning." In comparison with the control sample, ACR-3.87 [Fig. 9(b)] and ACR-5.76 [Fig. 9(c)] can postpone the time of PVC strips turning black. A further improvement can be observed in the strips containing ESBO [Fig. 9(d,e)]. The color of the samples containing ACR/$ZnSt_2$ turns black suddenly from a light yellow color. On the other hand, the color of the samples containing ACR-X/$ZnSt_2$ turns gradually from light yellow, to light orange, brown, and finally to black, which is similar to those stabilized by Ca/Zn with a high-Ca content.[6]

CONCLUSION

ACR-based ionomer with suitable ion content behaves as a good co-stabilizer to PVC. It is able to improve t_{ss} of PVC and postpone "zinc burning." FTIR spectra show that the ionomer can react with $ZnSt_2$ to form some new structures accounting for postponing "zinc burning." Usage of ionomer together with ESBO shows a synergistic effect on the stabilizing efficiency of PVC compounds containing $CaSt_2$/$ZnSt_2$ stabilizers.

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